

UNPUBLISHED PRELIMINARY DATA

ADHESION BETWEEN ATOMICALLY PURE METALLIC SURFACES

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Prepared for

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Supplement 1



SYRACUSE UNIVERSITY RESEARCH INSTITUTE

Department of Chemical Engineering and Metallurgy

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Semi-Annual Report

ADHESION BETWEEN ATOMICALLY PURE METALLIC SURFACES

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Submitted by:

Douglas V. Keller, Jr., Director

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SYRACUSE UNIVERSITY RESEARCH INSTITUTE

Department of Chemical Engineering and Metallurgy

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FOREWARD

This report is made up of two sections. The first section "Some Considerations of Metallic Adhesion Theory" is to be developed for a publication in the near future. The latter portion represents a short review of the experimental efforts underway presently, which, in general, are directed toward the confirmation of the views expressed in the theoretical section.

SOME CONSIDERATIONS OF METALLIC ADHESION THEORY

D. V. Keller*

INTRODUCTION

The term "adhesion" as it is applied to metallic systems probably involves a number of the same phenomenological fields and forces that are involved in the more common organic and inorganic adhesive systems; except for the complexing fact that the surface species in the metallic system is monatomic in behavior rather than molecular or polyatomic. As a consequence of this, as well as the very low oxidation state in which the surface metallic atom finds itself, the formation of an interface with some shielding species is a highly energetic event on a surface. This is exemplified by the large value of the heat of desorption of metallic cesium from a clean tungsten surface, e.g. 65 kcal/mole (1), or desorption oxygen from silicon which is about 230 kcal/mole (1). Coupled with chemical systems of this sort, other processes are also operative in metallic systems; for example, mass transport in the form of surface and/or bulk diffusion of the interfacial species; electrical energy transport in the form of electrical potential fields of quite sizable magnitude; compound formation, magnetic effects, and others. During solid-solid adhesion the problems of crystallographic orientation, defect structures, stress behavior, elastic and plastic deformation processes in the interface area are also involved. Each of these processes will have a direct bearing on the strength of the junction formed.

Fracture of this junction, on the other hand, is possessed with many of

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these same problems as well as the mechanics of fracture itself, e.g. stress concentration, etc. As a consequence of the complexity of fracture mechanism, the scope of this study will be limited to just the creation of a simple metallic junction rather than how the fracture of such a junction occurs.

Before becoming involved in an analysis of the details of the process, let us first clarify a bit of the history of the terminology of metallic adhesion and its relationship to the metallurgy field. The term "adhesion" was most probably extracted from the area of organic adhesives (2). In the metallic field, however, it actually signifies that two metal masses are welded together by some mechanism in which neither of the masses are necessarily brought into the liquid state. This "cold" welding process is aided either by normal or tangential forces (2), heat (3), vibrational energy, or the like. Magnetic fields as such have not been considered for the process, but, in all probability, they will also cooperate with the other fields and forces present.

Prior to critically examining the processes which result in the phenomena of metallic adhesion some limits ought to be placed on the system under examination. For example, if a metallic system is to be considered the surfaces in question must contain a majority of metal atoms in an oxidation state equivalent to that of the perfect metal-vacuum interface. Some authors (4) have arbitrarily chosen a surface represented by the value of less than 0.1 monolayer impurity coverage to represent the pure case. The necessity of this limitation is examined carefully in the chemical section. The attainment of such a surface condition for

experimental purposes is most difficult as has also been discussed by numerous authors (5,6), to cite a few. For example, the rate of monolayer formation at room temperature in a system at a pressure of 10^{-9} Torr is about 16 minutes, if an atomically clean surface was exposed to these conditions, the pressure remained constant during this period and that we can assume no bulk to surface diffusion has taken place. The loss of control of any of these variables may lead to rapid monolayer formation and as a consequence a complete change in the interface under examination.

Although the topic under consideration is metallic adhesion, referring to two metallic surfaces bonded physically to each other due only to the two interfacial atomic species, we must recognize that the oxides, sub-oxides, carbides, subcarbides, etc. that may constitute an impurity monolayer on a metallic surface can, in themselves, play a significant role in the adhesion process. This is evident in the tenacity of many bulk oxides to their respective metal substrates as the result of surface oxidation of the metal or as cited in the numerous experiments of Benjamin and Weaver (7,9) in which adhesion energies of metals and various inorganics were studied.* Since the chemistry of such species is most complex particularly in the small concentration which exist in monolayers, the presence or effects of these materials will not be considered.

The analysis of metallic adhesion may be developed in three separate stages consisting of those attractive forces and fields interacting

*Also (cf. page 11) McDonald et al.

between two metallic surfaces before actual contact is achieved, the chemical forces present after forceless contact at temperatures below the macro-diffusion range, and finally the effects of macro-diffusion and/or other energy activation processes. The first process may be considered as physical adhesion in a light similar to that of physical adsorption since the attractive forces are expected to be relatively weak forces due principally to long or short range dispersion forces not generally associated with the formation of a chemical bond. The range of these forces is limited from contact to a separation distance of about 5 microns. The second process, or chemical adhesion, is concerned generally with the formation of some form of short range chemical bond either covalent, electrostatic or metallic in nature across the interface with an associated decrease in free energy of the atomic species, which is larger than 5 Kcal/mole. The range of consideration is probably less than 10\AA . The necessity of the temperature and diffusion limitation in this case will become apparent in the more complete description to follow. The last general grouping brings together the effects of diffusion processes, mechanical working, radiation damage, etc. on a forceless contact. In experimental tests of adhesion all three categories are probably operative since the true contact area formed through the plastic flow of the surface asperities would expose some regions to pure metal-metal contact under a near forceless contact situation, while other regions reacted under the influence of the heat of plastic deformation and portions of the voids making up the difference between the observed contact area and the true contact area are within

the range of the fields of physical attraction. Thus, any theoretical or experimental examination of metallic adhesion ought to be cognizant to the magnitude and effects of all three processes.

PHYSICAL ADHESION

The physics and experimental evidence of the attractive forces between two macro surfaces at distances of separation in the micron range have been discussed by Casimir and Polder (10), Lifshitz (11), Sparnaay (12), Derjaguin and Abrikossova (13), Black, et al (14), and reviewed by Debye (15). The application of the dispersion force analysis to the processes of adhesion has been provided by Krupp, et al (16).

At intermediate distances of separation two parallel plates are attracted to each other by static surface charges, surface contact potentials and dispersion, or van der Waal's forces. According to Sparnaay (12), the experimental elimination of the effects of the first two forces are at odds since in order to nullify the static charges on two parallel plates, a circuit must be completed between the two surfaces, but when this is accomplished the two surfaces attract with a force (F) in dynes/cm² due to contact potential difference which is given by:

$$F = 4.5 \times 10^{-5} (V_1 - V_2)^2 / d^2 \quad (1)$$

where, $(V_1 - V_2)$, the potential difference is in mV and d is given in microns. Since a circuit is complete between two metallic surfaces in physical contact, i.e. contact junctions, this equation will be operative in the void spaces along the interface. It will not, however, be operative as long as the surfaces are insulated from each other, i.e.

before contact. Under these conditions the effects of van der Waal's attractive forces become important up to distances of separation in the order of microns. Two mathematical analyses of the attraction between parallel plates have been presented that, due to Casimir and Polder (10), was based on an approximation of perturbation theory applied to the electrostatic interaction of two dipoles, while that of Lifshitz (11) approached the problem in a macroscopic fashion. In the latter case, interaction was interpreted as being through the medium of fluctuating electromagnetic fields which are always present within and in close proximity to surfaces at all temperatures. Since the latter work has been extended (17) in a direction which will influence the interpretation of adhesion phenomena, a more careful examination of the significant parameters seems justified.

In a highly simplified form, i.e. "for practical purposes" (17), and for small distances of surface separation, l , (less than the wave length of the major adsorption frequencies), the force of attraction per cm^2 (F) may be represented as:

$$F = \frac{\pi \bar{\omega}}{8\pi^2 l^3} \quad (2)$$

where:

$$\bar{\omega} = \int_0^\infty \frac{(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3)}{(\epsilon_1 + \epsilon_3)(\epsilon_2 + \epsilon_3)} d\xi \quad (3)$$

and ϵ_1 , ϵ_2 and ϵ_3 are dielectric constants which are functions of an imaginary frequency $\omega = i\xi$, varying from the electrostatic value ϵ_0 (when $\xi = 0$) to one (when $\xi = \infty$). If the imaginary part of the dielectric constant (ϵ_1'') for real frequencies is known from experiment,

cf. reference 18, the ϵ_1 functions can be calculated from:

$$\epsilon_1 - 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon_1''}{\omega^2 + \xi^2} d\omega \quad (4)$$

where:

$$\epsilon_1 = \epsilon_1 \text{ or } \epsilon_2 \text{ or } \epsilon_3$$

and ϵ_1 , ϵ_2 refer to the solid surfaces, ϵ_3 refers to separating medium. Since the imaginary part of the dielectric constant is a material parameter, i.e. dependent on the number density of free electrons in a metal (18), the magnitude and behavior of the attraction is a function of materials constituting the system. For example, if both plates are of the same material, they attract each other at all distances irrespective of the medium between them. The force of attraction decreases monotonically with increasing distance. It is evident from Equation (3) that in the case of dissimilar metals $\epsilon_1 \neq \epsilon_2$, certain combinations will provide a force of repulsion rather than attraction, e.g. $(\epsilon_1 - \epsilon_3)$ and $(\epsilon_2 - \epsilon_3)$ have different signs in the essential frequency region.

Experimental evidence of these relationships has been provided by Sparnaay et al (12,14) and Derjagin (13) in the form:

$$F = - \frac{AS}{6\pi d^3} \quad (\text{non-retarded})$$

$$F = - \frac{BS}{d^4} \quad (\text{retarded}) \quad (5)$$

where:

F = attractive force

$A \sim 10^{-12}$ erg

$B \sim 10^{-19}$ erg cm

S = area of surface of flat plates

d in microns

and the transfer between the non-retarded and retarded law is expected (14) to occur at a distance in the order of the wave length corresponding to the major adsorption of the material. The agreement of the experimental data with these equations seems quite good for Quartz plates in a system under a vacuum in the range of 5×10^{-3} Torr. Although tests (12) were attempted between polished chromium, chromium steel plates and aluminum, the data did follow Casimir's equation for the first two; however, some difficulties were encountered with aluminum which indicated that the errors may be large. The surface oxide, for example, was considered as the cause for the small repulsions observed between the aluminum plates. No data has been reported for systems in which the metal surfaces are without contamination. Such a study, however, is underway currently in this laboratory.

Debye (17) indicated that extreme caution must be observed in the extrapolation of the above equations derived for long range force interactions from the micron separation distance range into the range of atomic diameters since the general field considerations used by Casimir and Lifshitz can no longer be considered as due to infinitely small instantaneous dipoles. Dzyaloshinskii, Lifshitz and Pitaevskii (17) have,

on the other hand, considered the van der Waal attractive forces for two parallel plates separated by liquids at various distances of separation and liquids in contact with a solid in a vacuum as indicated in Equation (2). The force of attraction follows a 1^{-3} law at small distances when the plates are separated by a liquid metal.

Following similar arguments the authors have examined the van der Waal's system of a liquid in contact with a solid plate in which the chemical potential of each surface was reduced into two components; i.e. that due to the bulk liquid and that due to the surface film (cf. chemical section). The latter was defined by the basis Equation (2) of the complex dielectric constants and thicknesses. Based on these arguments and criterion for bulk non-wetting and wetting and micro non-wetting and wetting were developed. The agreement of this analysis and the observed data for liquid helium were considered reasonable. The importance of this analysis should not be overlooked in that it provides a common basis for adhesion irrespective of the nature of the materials involved in the system, i.e. organic, inorganic, or metallic. The only requirement of the adhesion system in this case is that the electrochemical potential (Gibbs' potential (19)) is constant throughout the system for each component thereof. As we shall see later, chemical section, this requirement is often not attainable in some macro systems.

Krupp, Sanstede and Schramm (16) utilizing the Lifshitz analysis as well as a statistical mechanical approach as a basis, attempted to extend the more conservative works of Lifshitz to macro-solid metal systems in an attempt to obtain quantitative adhesion values. Although values

were obtained for the iron-copper system which ranged from $2-20 \frac{\text{mtons}}{\text{cm}^2}$, a great number of dubious assumptions were required which placed the quantitative nature of the analysis in some question. A more rigorous analysis would be desirable in which the complex integrations and assumptions are more clearly defined. The authors recognize that this type of analysis is limited to systems in which only the dispersion forces form the major bonding factor, even though it was applied to the iron-copper system.

In summary, it is evident that two solid bodies separated by small distances of vacuum are attracted by a force which follows a 1^{-3} law. The extrapolation of this law to longer distances, i.e. micron range, requires a modification to a 1^{-4} law, and to shorter distances, i.e. contact, the added requirement that the electrochemical potential of the ith component of the system remain constant throughout. Since adhesion is interested principally in this latter factor, a further comment seems justified. In a perfectly immiscible system the concentration of component b in a must, by definition, approach zero; as a consequence, excessive error should not be invoked if we assume that the mere presence of b in contact with a provides the conditions necessary for chemical equilibrium in the system, that is:

$$\bar{\mu}_b^B = \bar{\mu}_b^A \quad (6)$$

where:

$\bar{\mu}_b^B$ = electrochemical potential of atom b in phase B

$\bar{\mu}_b^A$ = electrochemical potential of atom b in phase A.

Under such circumstances, the contact potential forces and van der Waal's electromagnetic field forces are applicable and constitute the force of attraction. Furthermore, one would expect that the hypothesis of Dupré and Young as discussed by Zisman (*) in Equations (7) and (8), respectively:

$$W_{ab} = \gamma_a + \gamma_b - \gamma_{ab} \quad (7)$$

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (8)$$

where:

W_{ab} = work of adhesion

γ_i = surface tension

would be valid. An excellent analysis by McDonald and Eberhard (**) of the relationship of the work of adhesion to the relative energies of oxide formation for certain metals in contact with aluminum oxide has been provided. The suggested atomic model illustrates, in a relatively simple manner, the close balance between the van der Waal's forces and the electrostatic forces at the interface. If, on the other hand, the equality of Equation (1) is not valid in a contact system, the entire system may change particularly as the system temperature increases to allow for surface and bulk diffusion, as discussed in the next section.

CHEMICAL ADHESION

In an attempt to analyze the chemistry of various processes which may occur at an interface, particularly in the case of metals during adhesion processes, an atomic model for surface interactions was

* Zisman, W.A., "Contact Angle", Amer. Chem. Soc., R.F. Gould, ed., Washington, D.C. (1964) p. 1

** McDonald, J.E. and Eberhart, J.G., Trans. A.I.M.E., 233, 512 (1965)

developed (20), since in consideration of most metal systems the state of equilibrium is expected to be well removed from the state in question. That is, a concentration and an electrical potential gradient will exist in the system across the interface which may be eliminated only upon the attainment of total equilibration of the system, which, in turn, would change the system to an altogether different system.

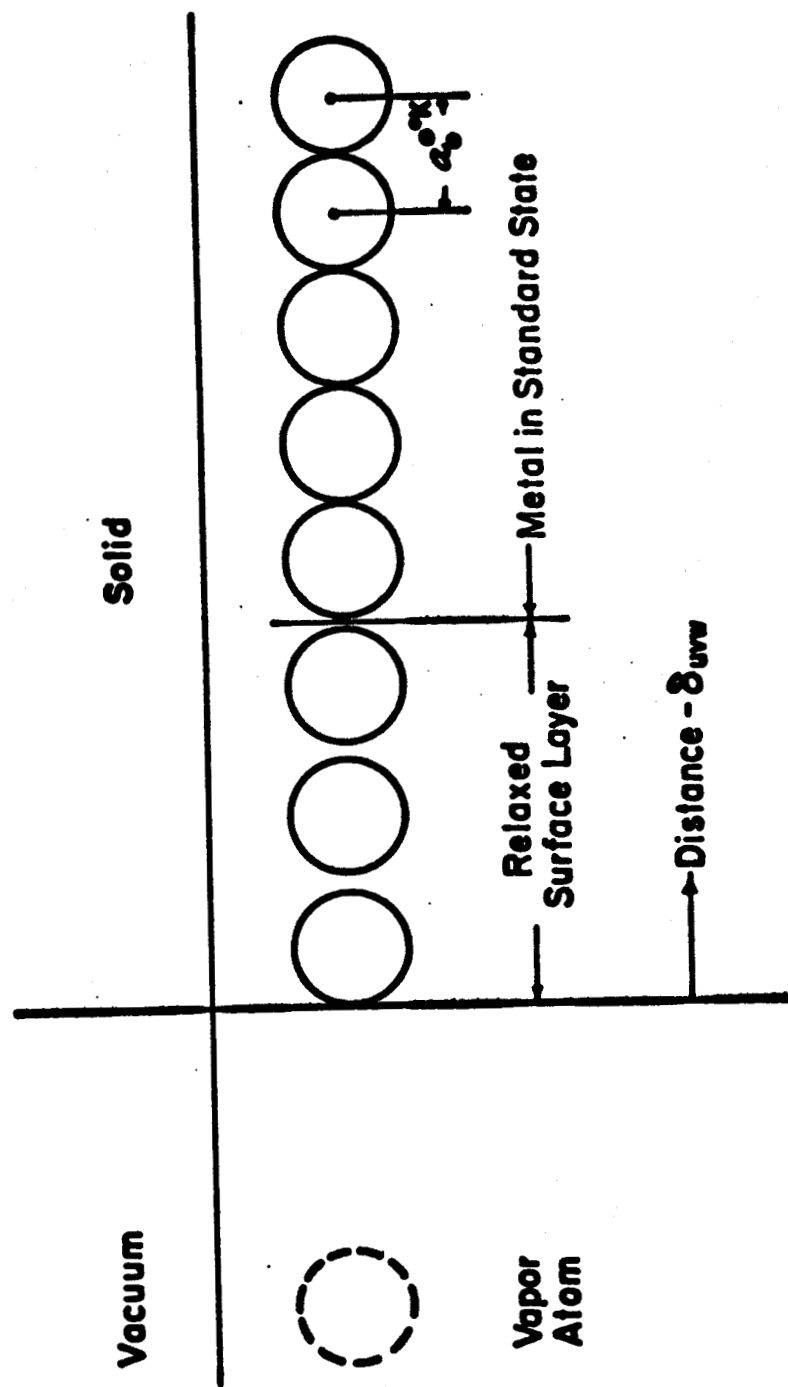
Generally, thermodynamics are utilized (21-23) to describe surface tension and surface free energy, which is adequate for the consideration of most macrophenomena; however, certain disadvantages of this approach will become evident in the initial stages of non-equilibrium interface formation and the subsequent diffusion phenomena.

The system under consideration is defined as a mass of pure homogeneous solid metal suspended in a perfect vacuum. Such a system will allow us to define the solid, its surface and the vacuum phase; thereafter, we can introduce impurities and other surfaces in order to view the resulting effects. Since we are particularly interested in the solid and its changes, the standard reference state for a metallic atom in this system will be represented by an atom in a perfect, unstrained crystal lattice at 0°K. Under such circumstances, it is presumed that all lattice sites are all occupied and can be represented by one of the standard point groups. For a first approximation, the existence and consequences of lattice defects in this system will be neglected even though their consequences may be included in such a model. Note should be taken that this approach is in direct opposition to the usual formulation given by physical chemists in which the free gas atom under

zero fields and forces is taken as the standard state. The convenience of the standard bulk atom will be apparent when alloys are considered.

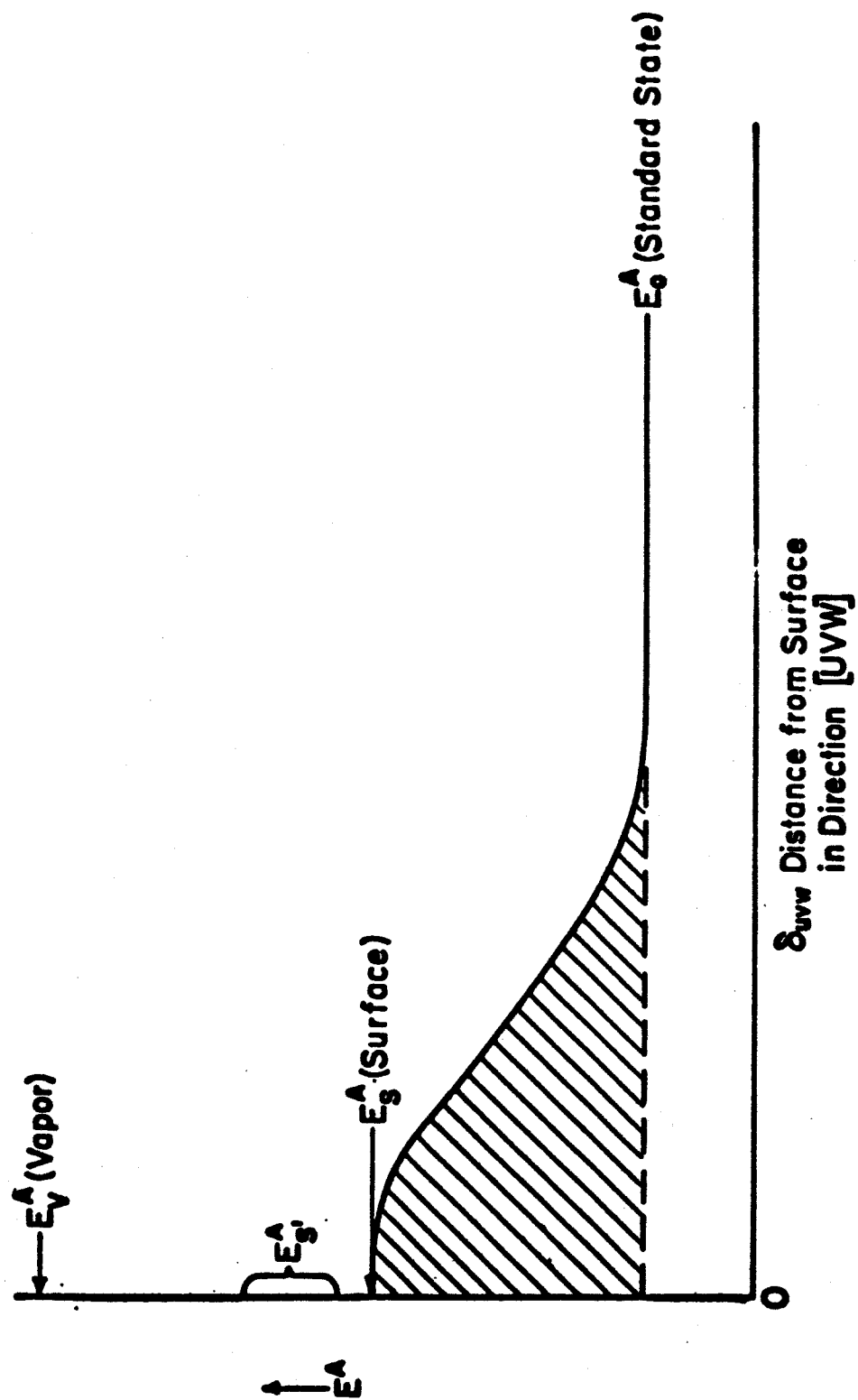
The energy of an atom, in this solid system infinitely removed from the surfaces, is considered as (E_O^A) or the atomic standard state of metal A. This energy value represents the total energy of the atom per unit volume, i.e. NE_O^A would represent the standard molar energy of the metal in question where (N) is Avogadro's Number. For example, one would have to add the heat of sublimation to an atom in this standard system to place that atom in the vapor state. All atomic energies will be referred to this state.

Let us now consider a linear chain model (24) of an equilibrium metal surface formed by a perfect vacuum-solid interface of a simple cubic metal such as that illustrated in Figure 1. At equilibrium some portion of the solid system will exist in the vapor state, according to the laws of the vapor pressure of A; some portion in the higher energy surface layers which are described by Gibbs (17) which is represented by a spacing between the atoms and the remainder as metal in the standard state. The value a_0 represents the unit cell parameters at 0°K of the particular crystallographic direction (uvw) which is normal to the surface plane. Since the energy values to be discussed are representative of all forces, physical and chemical, directional or non-directional, the energy value will represent the chemical binding forces which, to a degree, are directional as well as the strain energy forces which are set up due to the lack of nearest and next nearest neighbors in the surface plane. Because we have chosen the standard state as a



bulk atom which experiences attractive and repulsive forces from all directions in the crystal, the removal of a portion of these forces to form a surface atom, immediately places an unbalanced force on the surface atom which is to be accounted by a redistribution of the electron orbitals surrounding that atom. In effect, we have created a polarized atom which is at equilibrium with the system, but is somewhat unlike the bulk atom. The observation and effects of this polarization have been discussed recently by Müller (25) and Wallis (26) utilizing field evaporation techniques and studies of the Debye-Waller factor in surfaces, respectively. The depth of penetration of this "disturbed" region for the present will have to remain ambiguous as indicated by Park and Farnsworth (27); however, if we assume that these dislocated, or strained, atoms extend to three or four cells below the interface before the characteristic standard state is achieved, an excessive error will probably not be introduced.

Assuming that no excited state compounds are formed in the first few layers of the solid such as those formed in germanium (28,29,30), silicon (29), and carbon (30), and that the energy from the surface atom to the bulk state is a continuous function with regard to position from the surface, the atomic model can be placed in graphic form as shown in Figure 2. The graphical form suggested is not unlike that presented by Davies and Rideal (31) in their description of a water-oil interface or that utilized by Ehrlich (32) in his descriptions of adsorption phenomena. The change in energy ($E_v^A - E_o^A$) represents the atomic heat of sublimation at 0°K and ($E_s^A - E^A$) represents the heat necessary to excite a bulk atom



from the standard state to a surface site. The range depicted in E_s^A represents the high energy sites possible in the surface itself, e.g. edge, corner or planar in ascending order of energy.

The curve E_s^A to E_o^A represents the change in energy ($dE^A/d\delta$) of an atom as it is moved from a fully condensed site on the surface to the standard state. The total area under this curve (hatched) represent the total excess energy (σ_T) in the linear system due to the presence of the surface. Note should be taken that this value is not the same as the surface energy due to the surface atoms alone since it actually constitutes a three-dimensional value:

$$\sigma_T = \int_{E_o^A}^{E_s^A} E^A(\delta) d\delta \quad (9)$$

Since we have taken the energy value (E^A) to represent the total energy of the atom, the surface energy (γ) of the (100) planes of the whole solid in a simple cubic system can be represented by the equation:

$$\gamma_{100} = n_{100} \sigma_T \quad (10)$$

where n is the number of atoms per square per square centimeter. With the description thus far, it is apparent that as the crystal structure of the solid changes, say to body-centered cubic (bcc) from the simple cubic, just described, we will have to modify Equation (10) since the (100) planes of the bcc lattice involve atoms with two different geometries in the packing normal to the (100) plane. The change in packing will change the position of the (a_o) value in relation to the surface which, in turn, will produce two different σ_T values for one surface.

In such a case, the total surface tension will be:

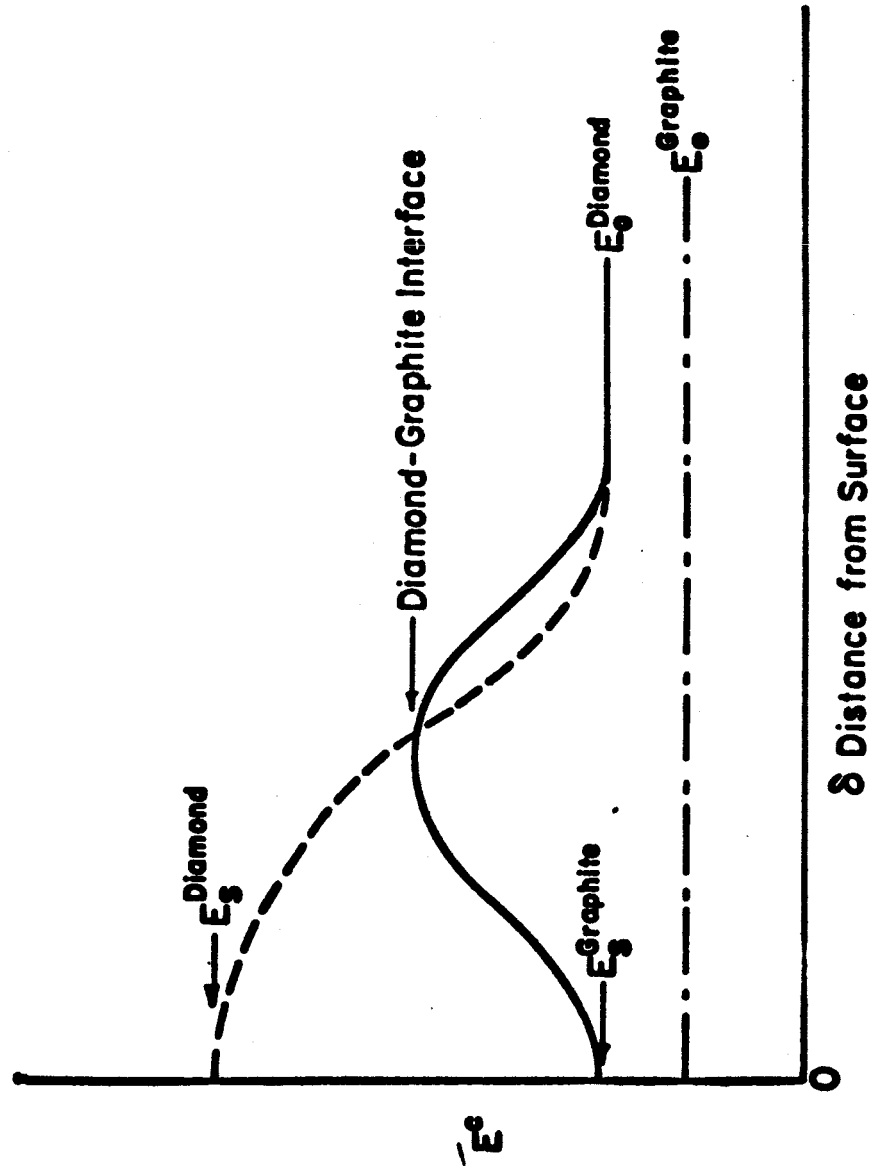
$$\gamma_{(100)}^{bcc} = N_{100}^x \sigma_T^x + N_{100}^y \sigma_T^y \quad (11)$$

where the x designates the cube edge packing and the y the body centered packing. Therefore, as the crystallographic direction is changed, the surface plane in question, atomic spacing, and number will also change, which in turn will modify the shape of the energy curve E^A illustrating the different values for the surface energy for the respective crystallographic directions. The variation of surface energy with crystallographic direction has been discussed by a number of authors (23,33, 34).

Another point which ought to be mentioned at this time is the fact that the surface energy of a solid is not a simple two-dimensional problem involving just the first layer of atoms. Such a model places limitations on an estimate of surface energy values which should be considered as the summation of the first layer excess energy plus the energy of the subsequent sublayers, which are also in an energy state above the standard state as indicated by Dzyaloshinskii et al (17). The limitations of which I speak are the suggestions that the surface energy of a metal must be some simple fraction of the binding energy (35,37) whereas in reality the surface energy is an excess energy in three dimensions of a region of atoms above the standard binding energy. As a consequence, a simple summation of broken bond energies in the surface layer only tells a part of the story. Experimental values of surface energies observed and discussed recently by Franklin (38) tend to bear out this interpretation.

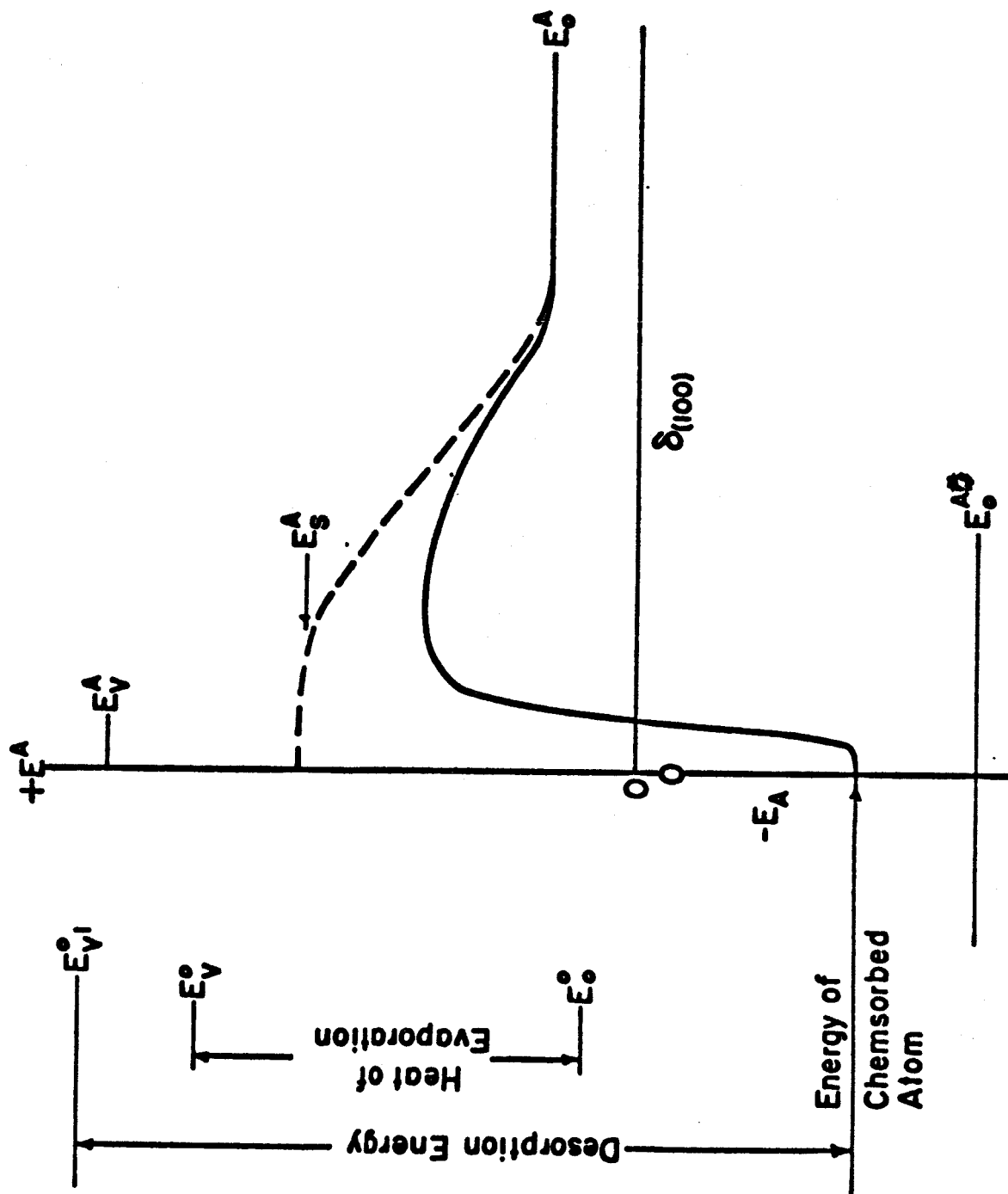
If the energy (E_s^A) is considered as a potential in the Gibbs sense, one immediately questions the state of equilibrium of the system we have just defined since the potential at the surface is not equal to that in the standard state; and by definition, these must be equivalent at equilibrium. The error is rectified if we realized that the energy described in the chemical "intuitive" sense in reality is only part of the energy involved; and the electrochemical potential equivalence requirement for equilibrium is concerned with all of the potentials in the whole system. Therefore, in the proposed model, if we recognize E^A value to be approximately the change in chemical potential (excess due to the surface) of the system in question, we also must recognize that a similar curve for a change in the electric potential must exist to maintain a constant electrochemical potential throughout the system. The change in electric potential at the surface is coincident with the valance bond and not the Fermi level as is in common usage in solid state physics as indicated in curves presented by Handler (39). Rather than probing these aspects further, let us examine the changes in surfaces which might alter the model.

Firstly, let us examine the changes which take place in our diagram if we consider a material such as diamond, which has a surface crystal structure (30) different from that of the bulk. Germanium and silicon demonstrate similar phenomena, but are less convenient since crystal modifications are not known. Figure 3 would represent the diamond surface if the diamond structure projected to the vacuum-solid interface. Under such circumstances, this would represent an extremely



energetic system since the unshared electrons of the surface atoms cannot readily form in-surface double bonds due to the geometrical arrangement, and also are unable to find available sub-surface sp^3 orbitals as these are full. Thus, to relieve the strain set up in this situation and the energetic favorability of the diamond-graphite transition, i.e. the sp^3 shift, a new surface phase is created which in turn must possess an interface with the original diamond structure. A diagram of this situation is shown in Figure 4 in which the energy lost by the transition in the surface layers would be the difference in the area under the diamond structure curve (E_s^{DIAMOND}) and that under the (E_s^{GRAPHITE}) curve. Since a graphite standard state is unlikely in such a thin layer the E_s^{GRAPHITE} does not extend to the standard state value of graphite (E_o^{GRAPHITE}). The hump in the latter represents the graphitic-diamond interface. Since the work to create a new surface ($\frac{dW}{dA}$) incorporates all of these changes, it would not seem invalid to presume that as a surface cleavage is propagated in a perfect vacuum, part of the energy of propagation goes into the activation energy of transition and the new surface, though not at equilibrium, will no longer represent the structure which was fractured. Silicon (29) and germanium (29,30) also present crystallographic species to the vacuum interface which are different from the original standard state structure. Whether or not more than one modification of various metals might be expected, is not known at this time as none have been reported.

The reversal of the above process in the case of carbon would appear to be unlikely since it would call for a reaction similar to the



inversion of the diamond-graphite transition, which is not only energetically unfeasible but rather difficult in a kinetic sense as demonstrated in the manufacture of synthetic diamonds. However, in the case of germanium and silicon, the surface forms are not known to be chemically stable compounds; therefore, the reversal may not be as unlikely as that in the case of carbon.

In effect, the complex graphitic-type phase of the diamond-vacuum interface is what has long been called the "disturbed" surface layer and as described is quite difficult to represent by classical thermodynamics. The difficulty arises from the apparent necessity for the use of a gradient to describe the chemical potential of the atoms in and near the vacuum-solid interface.

The redistribution of the so-called "dangling" bonds of the surface atoms as described in the carbon case, poses an even more complex problem in the case of metals since discrete orbital configurations of the atom and band structures of the solid, as proposed by Goodenough (40), may only be hypothesized. Utilizing these interpretations, however, in conjunction with the unit cell measurements provided through the results of low energy electron diffraction measurements, some insight may be provided. For example, if the unattached d, s, and p electrons exposed at a (111) nickel surface were to be accommodated only in the orbitals of the xy plane of the surface, one would expect measurable adjustment of the unit cell parameter in those directions which, according to MacRae and Germer (41), was not observed. They did report, however, an expansion in the lattice of about 5% in the z direction

normal to the xy surface. Although the experimental precision of the latter was contended by Park and Farnsworth (15) at a later date, the mechanism of interpretation remains open for further examination.

Another modification of the vacuum-solid interface is caused through the sorption of a foreign species on the solid surface. For simplicity, let us consider the monolayer adsorption of atomic oxygen on a surface of metal A and that AO is the only stable oxide of metal A, i.e. heat of formation of the oxide is exothermic. Again, our basic diagram to the right in Figure 4 illustrates the surface of A and its original surface energy, the area under the curve from E_s^A to the standard state E_o^A . For the gaseous phase the standard state is represented by (E_o^O) , the molecular vapor state by (E_v^O) and the vapor atomic state by (E_v^O) . Upon interaction with a surface atom of the metal, both the energy of the oxygen and the surface metal atom are decreased in approach to the standard state of the (AO) compound. This value is not attained because the combined pair on the surface do not constitute the compound standard state as defined, i.e. infinitely removed from a surface and the oxide, even if it were perfect would have an interface with the vacuum. In effect, the surface compound AO is in some excited state due to the lack of ordered nearest neighbors which would be found in a bulk system of AO . One should note that the surface energy of A has only in part been relieved by the chemisorption since strain between AO and A will still exist, and that the desorption energy of O also includes the excitation of the surface A atom back to its nude site in the surface. The equilibrium value E^{AO} might eventually be attained in the surface layer if sufficient

oxygen were present and diffusion allowed to progress to a point where pure single crystal AO could exist. This could only occur with the consumption of A and the movement of the strained interfacial zone in A toward the region of pure A at E_O^A .

The case of metal monolayer adsorption as presented in the adsorption-desorption energetics of silver from silver, molybdenum and nickel surface provides some very interesting relationships between surface phenomenon and bulk properties. The following desorption energy values are pertinent:

TABLE I

| | E_b |
|-------------------------|---|
| Silver Surface (42) | $\frac{2.90 \text{ ev}}{2.90 \text{ ev}}$ |
| Molybdenum Surface (43) | 2.2 ev |
| Nickel Surface (43) | 1.55 ev |

where (E_b) is the heat of desorption of silver from the indicated substrate. The data suggest that the silver atom is more closely held to the silver substrate than the substrates of molybdenum and nickel which seems to be in conflict with the atomic model of oxygen sorption which was just discussed. If, however, we consider that neither nickel nor molybdenum form any intermediate phases or solid solutions with silver in the bulk solid state, and work must be done on either of the two component systems to produce a mixture, the desorption data do indicate that the silver atoms would prefer to leave the molybdenum and silver system more readily than the silver system. Continuity is regained. The heat of desorption of gold from a molybdenum surface is given as 4.2 ev (43), which is in excess of that value when a gold surface is involved, i.e.

heat of evaporation of gold is 3.92 ev (42). These data suggest that a loss in energy takes place when gold atoms enter the molybdenum system, which is confirmed from binary phase data (44).

In effect, it is evident from the desorption data just presented that a free silver atom or monolayer film, on a nickel or molybdenum substrate, is unstable with respect to bulk silver; and if diffusion permits, the thin layer or atom will attempt to reduce the overall energy by forming a mass of least surface area under the influence of the contact potential and van der Waal's forces also present in the system. In the case of the gold at desorption temperatures, an equilibrium must be achieved by fixing the electrochemical potential constant throughout the three phases; that is,

$$\bar{\mu}_{\text{Au}}^{\text{vac}} = \bar{\mu}_{\text{Au}}^{\text{surface}} = \bar{\mu}_{\text{Au}}^{\text{bulk}}$$

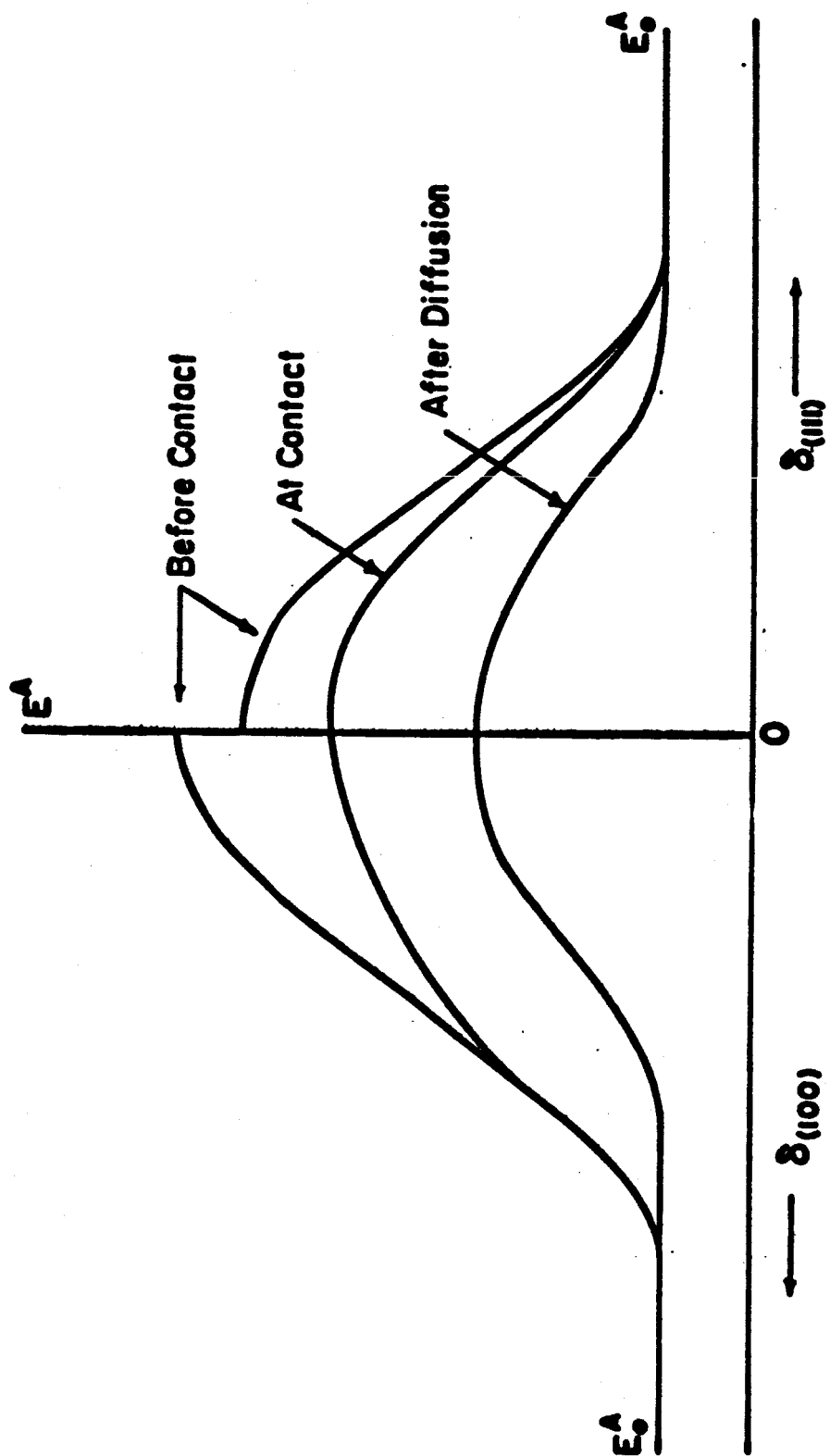
which requires a larger energy of desorption since an attraction between Au and the matrix is evident.

If this model is correct at this point, we can readily see why a sessile drop of one metal (A) would not spread on a second metal (B) even though the surface energetics ($\gamma_a < \gamma_b$) seem to be favorable and the formation of a monolayer of A on B substrate is possible. The indium-aluminum system has been studied (45) under these conditions and seems to follow the proposed mechanism. In the consideration of immiscible systems of this sort, extreme care must be utilized in the definition of the immiscible phases with regards to the percent solubility at a specific temperature since most immiscible phase systems will, at

some temperature, become miscible.

Due to the extreme difficulties in attaining large numbers of reliable desorption energy data of various metal atoms from various metal substrates in the absence of interfering impurity reactions, the data necessary to extend the above relationships into other metal systems is not available. The data from other inorganic reactions, however, seem to substantiate an interpretation of this type.

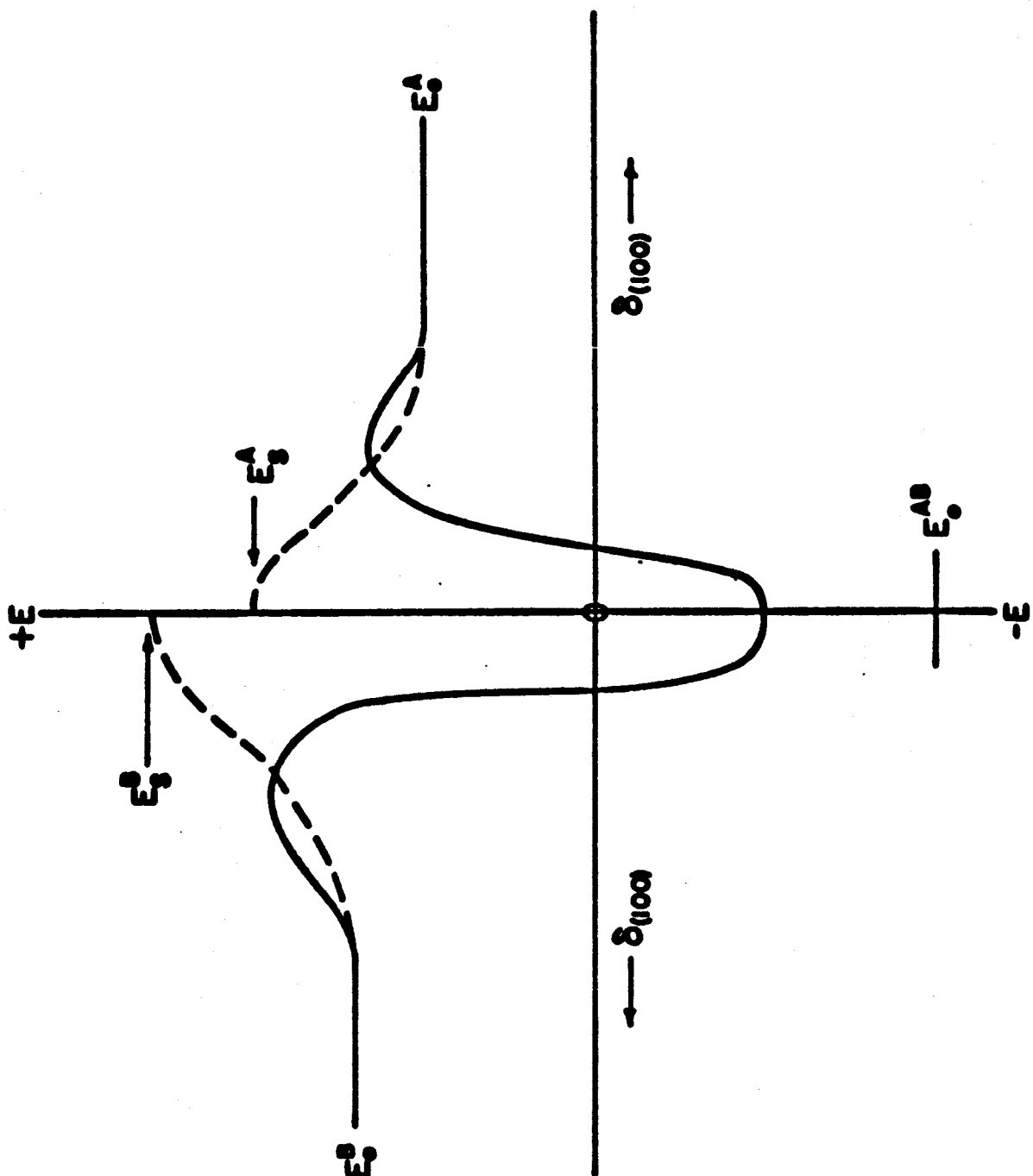
Since the formation or destruction of the vacuum-solid interface by means of a second solid body does involve the conditions of the free vacuum solid interface per se, the proposed model would have to be invalid if continuity were not maintained throughout such interfaces. Let us next, therefore, consider the formation of a grain boundary by two metal crystals of different crystallographic orientations, i.e. surface energies are different but the standard states in each case are the same since the standard state was defined as a volume energy. Upon initial contact at 0°K as illustrated in Figure 5, we will have a non-equilibrium situation in which the surfaces are held together by dispersion forces and some atomic bonding only when the particular interfacial atoms are aligned properly to utilize their neighbors' atomic orbitals. This could be considered as an accidental alignment, whereas after surface diffusion is allowed to take place the system further reduces its energy by readjusting the interfacial atoms to suit the new nearest neighbor field, which has replaced the vacuum phase and in turn reduces the system energy to a minimum. Since the atomic arrangement is different in the new phase, some strain energy must remain in the



interfacial region to account for this. It is interesting to note that this description conforms to the famous work of adhesion (W_{ab}) equation presented so many years ago by Dupré (47) as shown in Equation (7). A portion of this interfacial energy can be represented by a defect structure model based on the original arguments of this model; however, due to time limitations, we shall not consider the effects of defect structure in this discussion.

To this point, the proposed model of a surface has been designed to coordinate with known phenomena and re-explain mechanisms which have been discussed and accepted by many authors. The next obvious step is to expand this model to include a solid-solid metal adhesion interface between two dissimilar metals as that which might exist in a vapor plating experiment.

Consider the effects of two bulk metals A and B in contact which, under equilibrium conditions, form only one intermetallic compound (AB) by an exothermic process. Following the patterns set down in the previous examples, we can draw an energy diagram for the instant of contact as shown in Figure 6 in which the standard states of pure A, pure B and pure AB are designated as E_O^A , E_O^B , and E_O^{AB} , respectively; and the surface energies of surface A and B atoms are E_s^A and E_s^B , respectively. As in the case of the sorption, one would not expect the interfacial compound to be in a true state of equilibrium (E_O^{AB}) due to the lack of thickness of the compound and to the strain of orientation with each of the original phases. Again we must remember that we are assuming ideal forceless contact of planer surfaces at a temperature in



which surface diffusion may be involved; but, bulk diffusion is not concerned.

The validity of the Dupré equation in a system such as this is still correct if the broadest of definitions for the interfacial energy are accepted and the recognition that the use of equilibrium values are no longer meaningful is made.

Before we leave this diagram, let us first analyze what we might expect of such a system if the temperature were increased to a point which would allow bulk diffusion. In order to simplify our discussion, let us presume that a molar mass of A is equal to that of B and that at system equilibrium the entire mass will be at E_O^{AB} or thereabouts. In effect, we are asking for an energy decrease of $(E_O^{AB} - E_O^B)$ for the mass of B and $(E_O^{AB} - E_O^A)$ for the mass of A. This constitutes the total driving force for diffusion toward equilibrium; however, in the mechanics of attaining equilibrium A and B atoms must be excited over a strain energy barrier and diffuse through the mass AB before they can get together to expand the zone of excited AB. Due to the differences in relative standard states, diffusability through these fields and gradients and the simple geometry of the system diffusion across such an interface is capable of some very interesting phenomena as demonstrated by the observations in Kirkendall type experiments (47). For example, voids on one side of the interface may be created by one of the atoms diffusing out of that region and not being replaced by its counterpart. After a period, these vacancies may accumulate and a void is created as observed in some of the experiments conducted by McEwan

and Milner (48). Another occurrence which has been called "Mantano interface" is in effect a very sharp chemical gradient well removed from the original interface. Thus, the events in and around such a diffusion interface are characteristic of the particular species and most difficult to predict except by direct observation.

Based on this model, one would then predict that the strength of the chemical bond across an interface to be a function of the nature of the equilibrium phases which can occur between the two metals under ideal conditions. Thus, one could assume that the composition gradient across an interface region could be represented crudely by the phase diagram of the components at that particular temperature and the amount of phase present restricted by the ability of the pure species to diffuse through the interface region.

The existence of the chemical potential gradients in such metallic interfaces are most apparent as are the electrical potential field counterparts, particularly if the coupling of these two fields are considered, e.g. contact potential differences and the general phenomena surrounding the thermoelectric behavior of materials. The examination of chemical and electrical properties of semi-conductor interfaces such as the epitaxial interface between germanium and silicon, indicates that the proposed atomic model is consistent with experimental observations (49). The interface between silicon and germanium apparently accepts the 4% difference in lattice size as an interfacial strain energy, which in turn affects the shape of the conduction and valence band in the interfacial region.

Next to be considered are metal couples such as silver-molybdenum or silver-nickel interfaces which are immiscible at the temperature range in question. Thermodynamically, under ideal conditions, these systems require work, or energy, to form mixed phase or to permit diffusion to take place. That is, the hypothetical mixture has a E_0^{AB} value greater than either E_0^A or E_0^B . If the amount of work necessary to create a chemical bond across the interface is greater than the energy lost in surface energy decrease, then it is apparent that no chemical bonds should form and in the ideal situation strong bonding of the two bulk sections should not exist. Will contact potential or van der Waal's adhesion exist? This is difficult to predict for metal systems at this time, as indicated in the previous section, for we have no experimental verification of the field forces in between pure metallic surfaces in contact. Under certain conditions, however, one could imagine a case in which the interface was mechanically worked to a high degree, and thus by increasing the energy states of the surface atoms to a point such that interface formation would be energetically feasible as indicated in the following section.

The atomic model representing the vacuum-solid, gas-solid and solid-solid interfaces discussed above, must be considered only as a first approximation to the actual events that take place at interfaces since only a uni-directional model has been examined. The existence of surface diffusion, increased bond strength in the xy plane direction, polarization effects and numerous other phenomena, which were not considered directly, will contribute in varying degrees to

any one specific mechanism or property under consideration. The purpose of the proposed model was to establish a common denominator for surface phenomena in that while considering one particular experiment, the investigator is not apt to lose sight of the similarities that exist with other surface phenomena. An extrapolation of this model into the energetics of vacancy formation and condensation as well as surface properties of ultra-fine particles is underway with some degree of success, which suggests that the limitation to macro surfaces is not necessary.

MECHANICAL EFFECTS

The effects of temperature on a theoretical adhesion system was reviewed in the previous section; however, the possible effects of mechanical working and other mechanisms which might raise the general level of the interfacial energy, have not been discussed. Before considering these as a general case, a degree of insight is provided through a review of the macro-adhesion experiments, which have been reported in the literature. Although there are a number of related studies in the fields of powder metallurgical processes, explosive bonding, vacuum friction and outer space lubrication studies, a complete review of these aspects at this time would seem beyond the scope of this paper.

Since the contributions of the Surface Physics and Chemistry Department of the Cavendish Laboratories, under Bowden and Tabor (2,3), have probably produced the most exhaustive studies in the area of solid adhesion, let us first examine their interpretations. Based upon more

than thirty years of friction and adhesion studies, they conclude that metals will adhere unless adsorbed gas films and oxide surface impurities interfere with the contact of the metal substrates or when the normal load is released the released elastic stresses present in the interfacial area are of such magnitude as to rupture the adjoining interfacial welds. That is, adhesion of clean surfaces is proportional to the normal load and independent of the size of the bodies in contact.

Let us examine the cleanliness of the surface and its effect.

Figure 7 depicts the appearance of a typically polished metal according to Samuels (50), which has been modified to include the sorbed gas layers. Accordingly, metals in a polished condition under a small load contact are separated by gas layers and/or oxide layers. The substrate metal atoms rarely affect intimate contact. As the load is increased, the fracture of the oxide and consumption of the sorbed gas on the exposed metal areas increases the probability of metal-metal contact. Naturally, surface irregularities, asperities, during slip may further increase this probability even under low loads.

The effect of surface cleanliness on the coefficient of friction was demonstrated by Bowden's group (2) and is shown in Figure 8. The coefficient of friction (μ) reflects the adhesion effect in that μ is regarded as a sum of mechanical force of shear due to surface roughness plus the force of shear of contact welds. In this case, the contacts were Pt, Ag and Ni which had been degassed at various temperatures in a vacuum of 10^{-8} Torr. In this set of experiments, platinum was the only metal to show complete seizure (1200°C) without first cleaning the

Figure 1
Surface of Typically Polished Metal
Samuels(5)

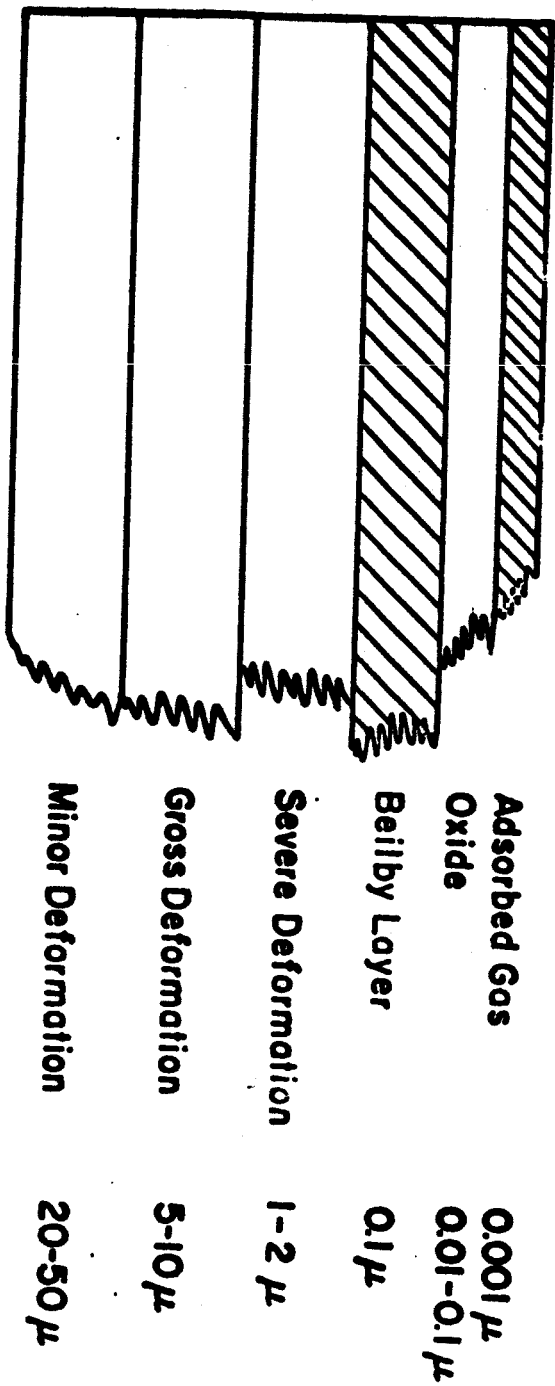
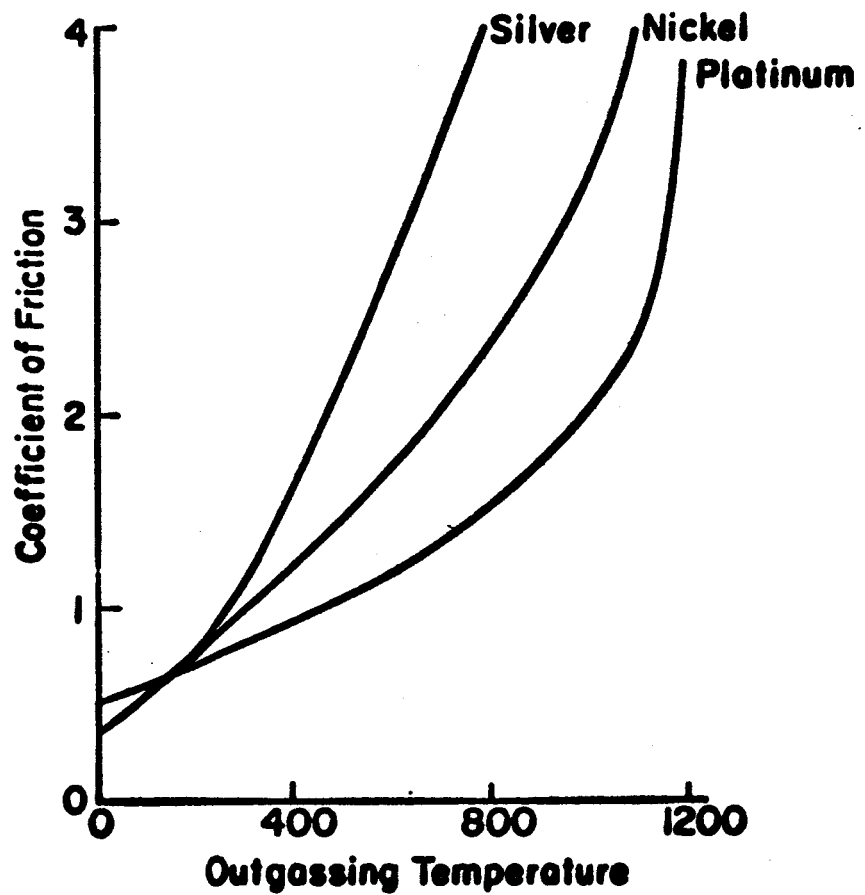


Figure 8
Room Temperature Friction After
Various Outgassing Procedures
Bowden (2)



surface by a gross evaporation process.

Bowden contends that the effect of tangential stresses in the contact area are almost as significant as the surface cleanliness. For example, the coefficient of adhesion, i.e. the ratio of the adhesion force to the junction forming force for simple clean metals, is about one to four, while the ratio is much greater than this when a tangential stress is imposed on the system.

Let us examine some of the details of junction growth under the influence of the combined stresses. The impression of a hard spherical metal sample into a flat metal plate (as shown in Figure 9a) with a load (W) to create an impression of diameter (d_o) is related to the yield pressure (p) of the plate through the equation:

$$W = 1/4 d_o^2 p \quad (12)$$

If the load is removed, the sphere and the plate will recover elastically as shown in Figure 9b, so that, according to Hertz, the radii will be related in the following way:

$$\frac{1}{R_1} - \frac{1}{R_2} = \frac{11 W}{2E d_o^3} \quad (13)$$

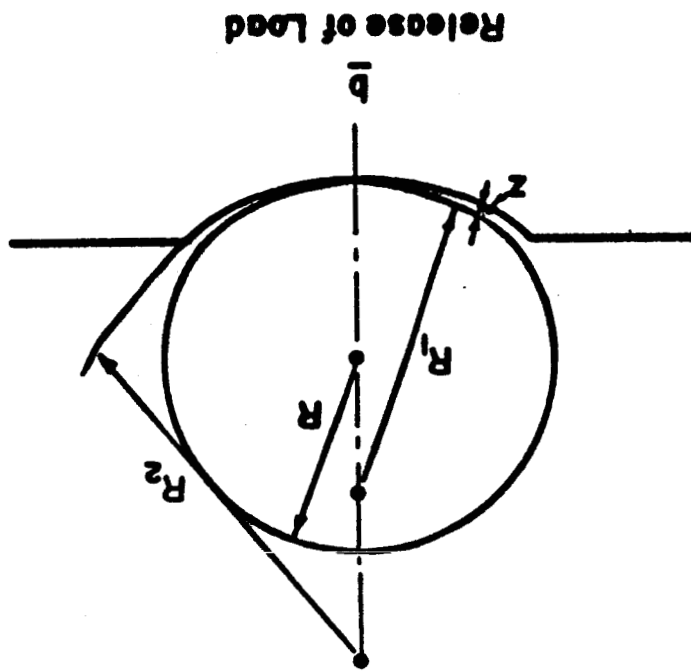
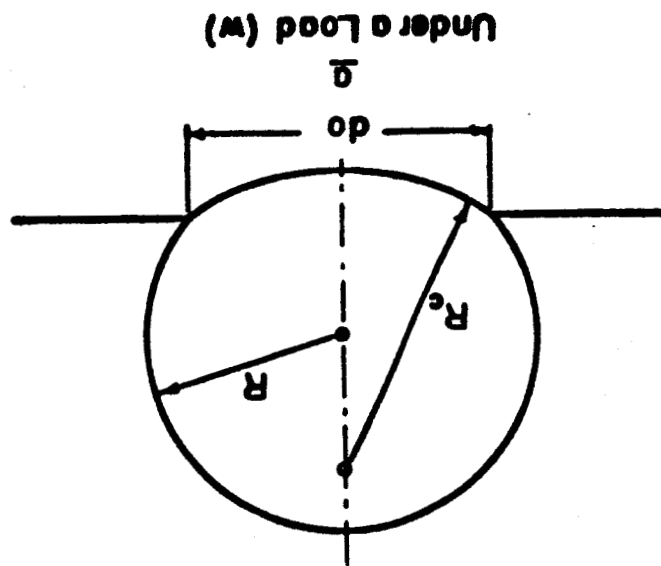
where E is Young's Modulus of both bodies and Poisson's ratio is 0.3.

The assumptions necessary for such model include: contact over limited area; metals welded together in small bridges; total cross-section area proportional to load or if no released stresses are present (force to break bridges).

However, if elastic stresses are released contact radii of the

Theoretical Model of a Sphere Interacting with a Surface

Figure 9



indenter and the indented will change, and such stresses will in turn subject the weld bridges to an enormous tensile load causing their fracture if the material is not fully ductile in nature. By expanding this model using plasticity theory, Bowden has further shown that the ratio of the adhesion with the application of tangential stress (σ) to that under static conditions (σ_0) is related to the cube of the ratio of the contact diameters, respectively, and to the tangential stress coefficient (μ) as shown in Equation (2).

$$1 + \alpha\mu^2 = \left(\frac{\sigma}{\sigma_0}\right)^{4/3} \quad (14)$$

where α is an empirical constant. Equation (14) is illustrated in Figure 10 which agrees reasonably well with the observed data which is not shown in graph. The static coefficients of adhesion (σ_0) for the observed data are shown in Table II:

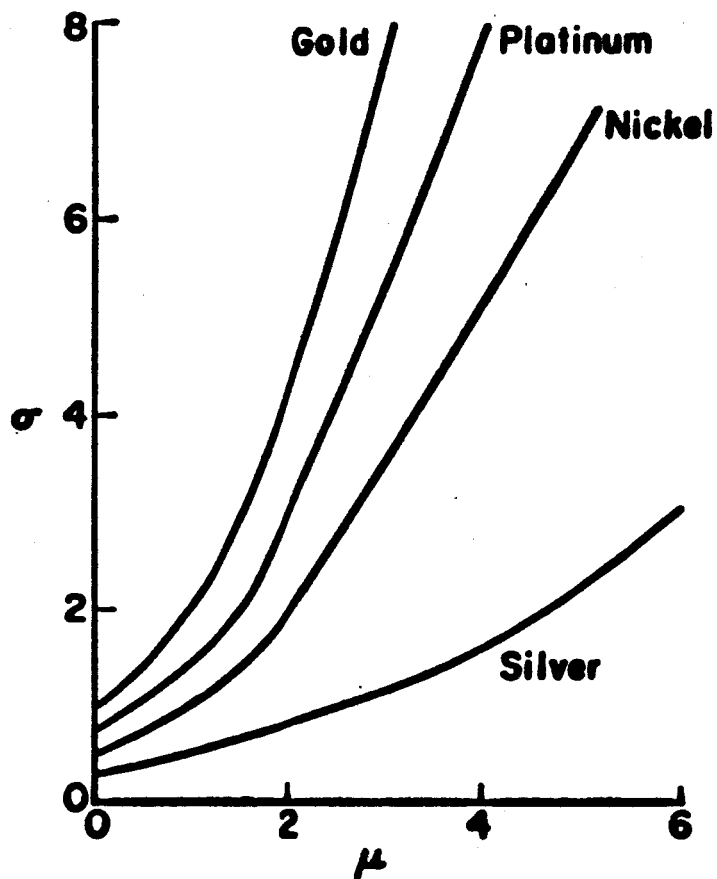
TABLE II

| <u>Coefficients of Adhesion</u> | |
|---------------------------------|------|
| Gold | 0.62 |
| Platinum | 0.45 |
| Nickel | 0.30 |
| Silver | 0.11 |

The empirical constant (α) was 3.0 in all cases. Pure static adhesion values were not used because the accuracy of measurements were too low and very susceptible to impurity layers.

One of the other more interesting contributions to the mechanism by Bowden's group is the effect of temperature on adhesion couples.

Figure 10
Coefficient of Adhesion (σ) versus
Tangential Prestressing Coefficient (μ)
Bowden (2)

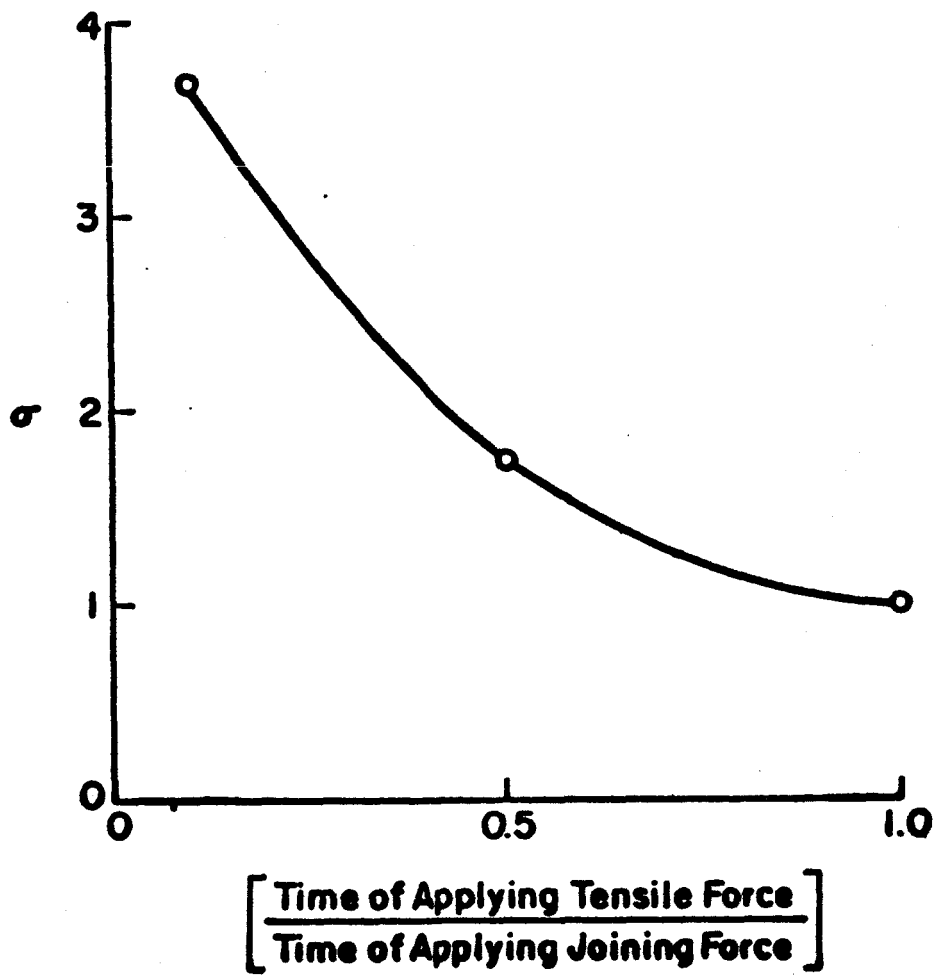


Utilizing static loading of clean platinum surfaces at about 730°C, they observed that creep is more significant in increasing the contact area than mass diffusion at the interface than other modes of mass transfer. Figure 11 presents the change in adhesion coefficient as a time effect. Temperatures in the range of $0.5 T_{mp}$ also should have an effect by annealing the work-hardened "bridges"; and as a consequence, increase the adhesion strength.

In summation of the work at the Cavendish Laboratories which obviously is directed toward adhesion as it affects the process of friction, we can say that two major factors influence metallic adhesion, e.g. impurity films which prevent metal-metal contact and excessive elastic forces within the contact area which, when released, tend to rupture the adjoining bridge welds across the interface. Furthermore, adhesion can be represented by a coefficient of adhesion which is about equal to one unless tangential forces are present and then the values may be much larger than one. Micro-analysis' of the systems are not considered in detail.

The application of extreme tangential or rotational stresses by forcing two large specimens of metal together either by compressional loading, punch-bonding or rolling mill methods can be interpreted as an extension of Bowden's work on extremely small tangential stresses. In effect, the macro contact forces are used to break up the gas-oxide interface in a manner such that the underlying metal phases are worked into a position of clean metal contact. Two major groups have contributed in this field and an examination of the data on twist-compression

Figure 81
Effect of Creep on Adhesion Coefficient (σ)
Bowden (2)



bonding by the Bell Laboratories group (51,56) and roll-bonding by Industrial Metallurgy group (57,62) at the University of Birmingham will provide some insight into the metallurgical factors which will be of concern once the metal atoms at the interface are brought into contact.

Sikorski's apparatus for twist-compression (51,53) is quite similar to that previously described by Anderson (54,56) and consists of the compression of a quarter inch metal rod into a 1/4" OD x 1/8" ID tube of metal and further applying a torque or a 180° twist to the compression junction. The data are recorded as a median coefficient of adhesion (MCA) which consists of a statistical analysis of a number of runs on the same metal pair. Again the coefficient of adhesion is the ratio of the force of adhesion to the loading force. The large scatter of individual data points is expected due to the extreme interface work performed in attaining a large percentage of metal-metal contacts; however, the mean coefficient of adhesion produced from the final analysis of all the data points for one metal-metal couple is said to be reproducible to about 2%. On this basis, the relationships from metal to metal should provide a good comparison of what should be expected if adhesion were performed under more ideal conditions. Since the junctions are formed under the conditions of extreme normal and tangential forces, the condition of the initial surfaces has little effect on the outcome of the experiment, unless, that is, heavy grease residues are present which act as a lubricant for the system. Simple filing of the surfaces is the usual practice. Essentially, as long as the twist-compression forces are capable of rupturing and distributing the oxide and gas layers

Mean Coefficient of Adhesion

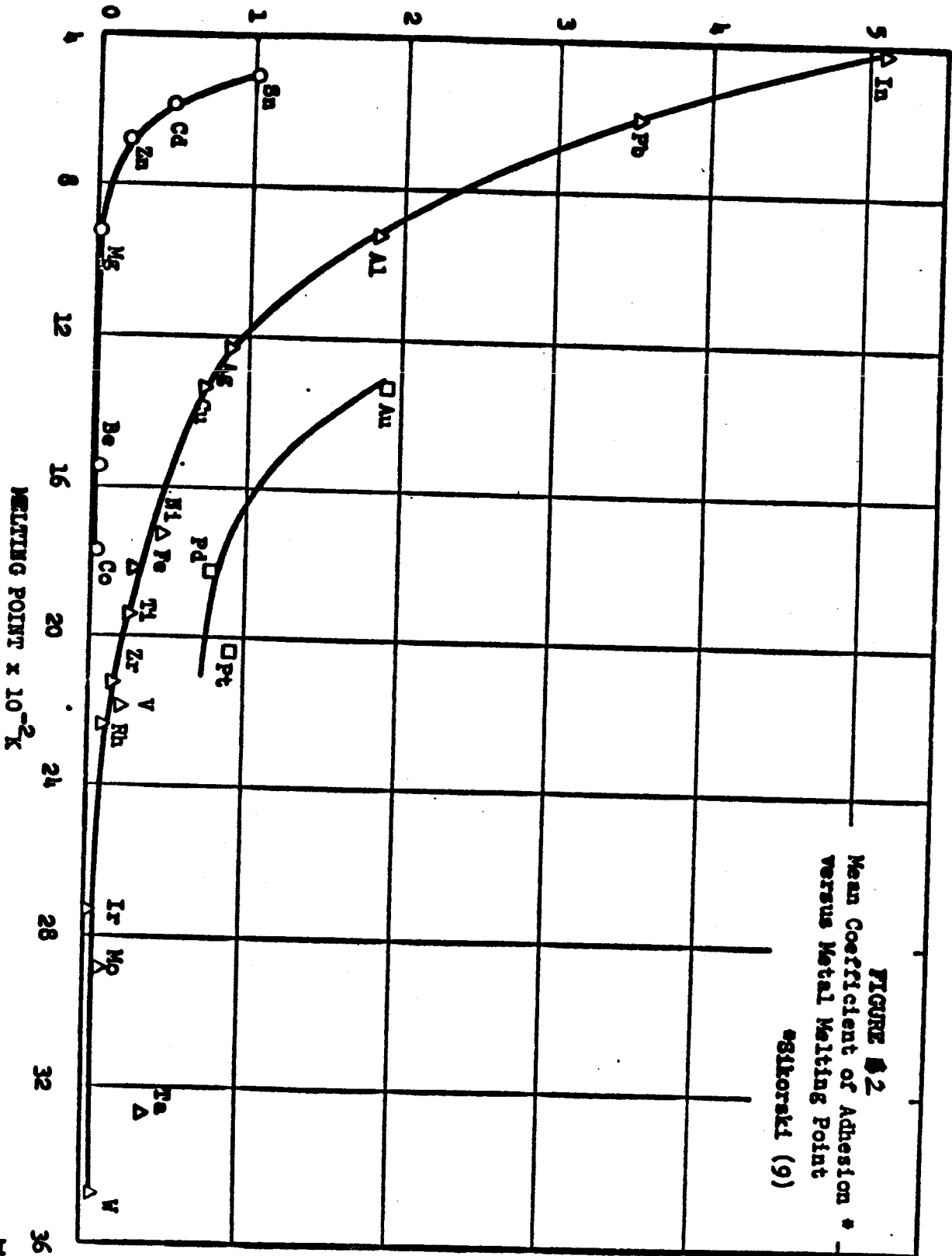


FIGURE #2
Mean Coefficient of Adhesion *
versus Metal Melting Point
Sikorski (9)

iron-silver system (immiscible) was found to be 0.006 while that of the copper-aluminum system (miscible) was 0.60.

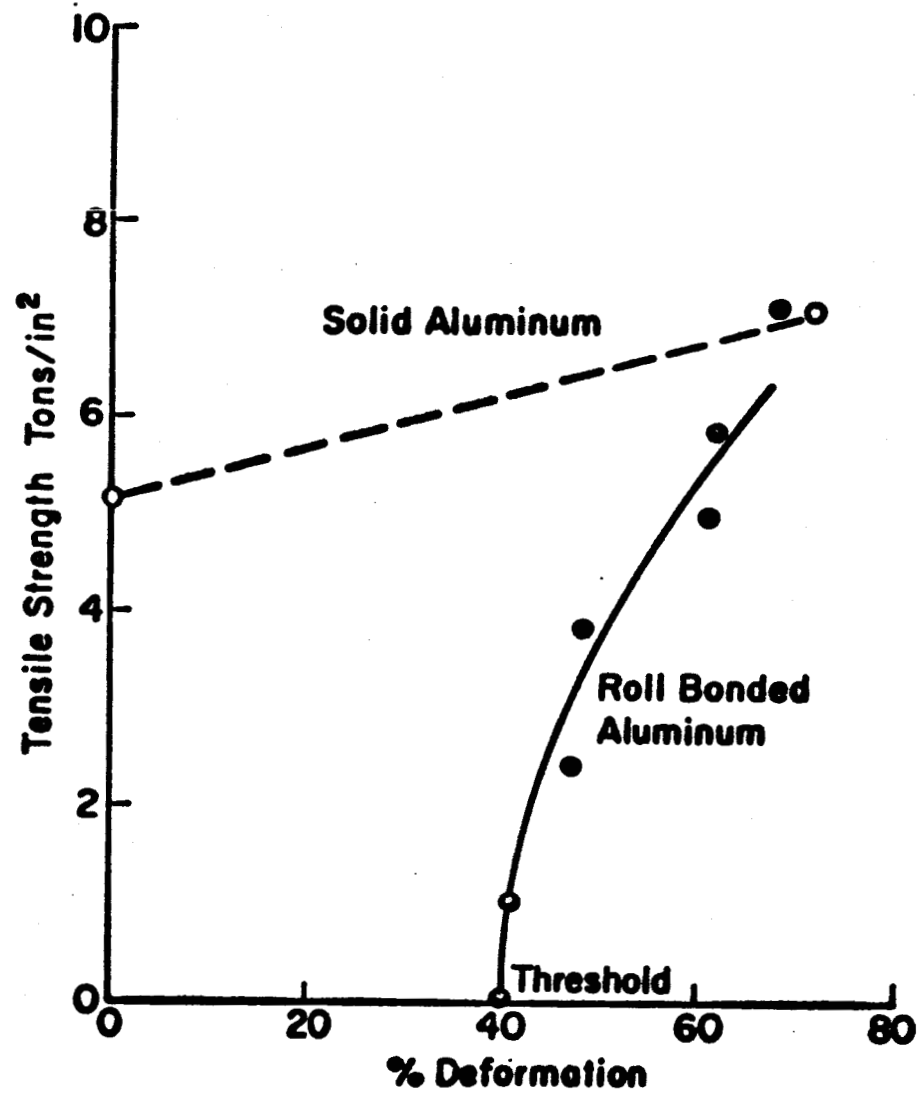
In conclusion, we have seen a confirmation of the necessity of surface cleanliness plus the additional effects of crystal structure, hardness, melting point, surface energy, and composition on the ability of an adhesion weld to form between two metals. Before we attempt to accumulate these various factors under general headings and analyze critically their ramifications, let us examine one other major effort in this area to examine some of the other metallurgical effects.

The group of researchers under Milner and Rowe (61) have been examining an adhesion system similar to that of Sikorski's in that the metals are forced together under extreme loads and the resulting bonding observed. Milner's system involves the composite rolling of two samples in a rolling mill to some degree of deformation $\left(\frac{\text{upset area} - \text{original area}}{\text{original area}} \right)$ under conditions in which the composites are not permitted to move with respect to each other. From the rolled composite, a sample is cut such that the resulting interfacial strength is tested as a pure shear specimen and the strength values compared to a pure metal specimen or the pure weaker component of the composite.

Again the surface cleanliness is of major importance; and, in fact, it seems to be a controlling factor in the hcp metal systems. Generally, the samples are coarse-wire brushed, brushed and held in an inert atmosphere or brushed and held in a vacuum (10^{-6} Torr) shortly before they enter the rolls. The resulting data for a series of tests on aluminum at various degrees of deformation are presented in Figure 13. As the precautions to prevent recontamination of the brushed

Figure 13

**Room Temperature Pressure Welding
of Aluminum**



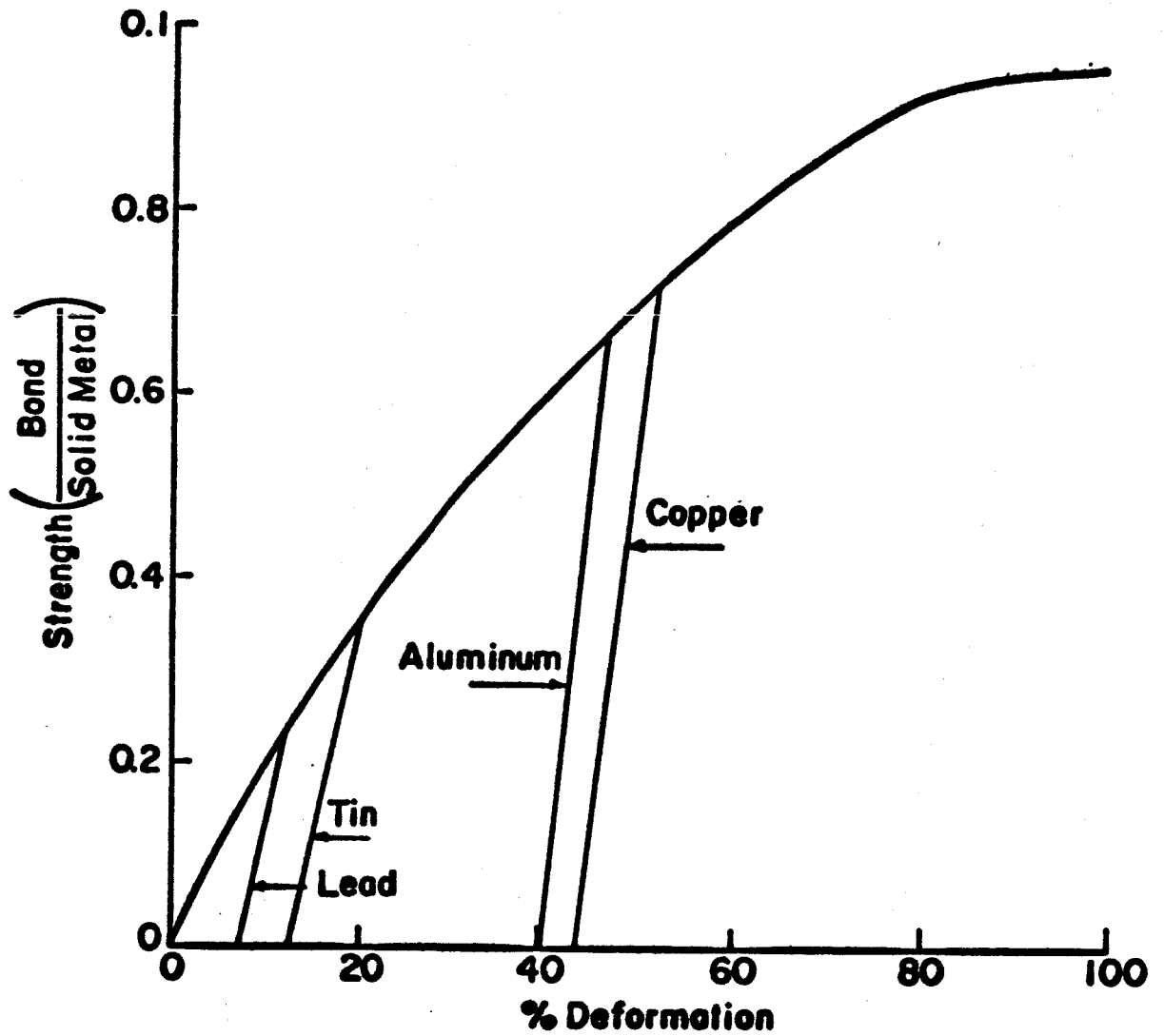
surfaces are improved, the threshold deformation for the onset of adhesion decreases. Recently, Rowe (62) indicated that this has been decreased in an exceedingly good vacuum to about 2%.

The mechanism of adhesion proposed by this group depends strongly on the interaction and behavior of the oxides formed by the materials rather than on the materials themselves. They suggest that if the oxides are compatible and tend to adhere to each other during deformation, and, as a consequence, break up as a unit layer, more of the substrate metal junctions will be formed and the junction will be stronger. The complex slip systems of magnesium and zinc tend to permit the breakup of the surface oxides in a heterogeneous manner, thus preventing metal-metal junctions from forming which result in weaker composites. Therefore, the only effect of the rolling is to expand the unit surface and unit oxide coating under conditions in which the oxide itself cannot expand, thus providing clean metal-metal contact. In other words, an increase in deformation yields an increase in strength as shown in Figure 14. The effect of temperature on such a system tends to decrease the required threshold deformation except in the cases in which the oxide is soluble in the metal. In such cases, (Fe, Cu, Be, Ti, etc.), an increased bonding strength occurs at the higher temperatures. They also noted the relationship of bondability from metal to metal to the respective melting points. Generally, the more impure the bulk metal system, the poorer the bonding which was confirmed by Sikorski.

The most interesting results of the roll-bonding studies, however, occurred when dissimilar metal pairs were rolled as composites and tested

Figure 84

Strength of Roll Bonded Material as a
Function of Percent Deformation



or subjected to a post-heat treatment and then tested. The immiscible metal composites, Cd-Fe, Fe-Pb, Cu-Pb, and Cu-Mo, were all subjected to a deformation greater than 50% and the resulting junction strengths approached a value near that of the weaker metal in all cases. This is in direct contrast to the observations of Sikorski and as we shall see later to some of our own observations. The fully miscible systems investigated included: Cu-Ni, Fe-Ni, and Mg-Cd. At 75% deformation in the Cu-Ni system, the strength approached 80% of that of Cu while a 500°C post-heat treatment increased the strength of the junction to nearly that of copper. However, a 1000°C post-heat treatment of the same system caused the junction strength to decrease to less than half its original value due to the occurrence of diffusion porosity. The Fe-Ni samples also showed porosity with post-heat treatment. The Mg-Cd sample yielded a bond strength of only about one half of that of Cd, which remained constant even after a long duration heat treatment at 300°C, which also caused extensive interdiffusion across the interface. Fracture was always along the original interface.

The partially miscible systems considered involved the Cu-Fe, Cu-Ag and Al-Zn systems. The Cu-Fe and Cu-Ag systems provided a good cold weld and improved their strength to that of the weaker metal with post-heat treatment. The Al-Zn system yielded a poor weld and further weakened due to porosity upon diffusion in the post-heat treatment cycle.

The systems Cu-Al, Fe-Al, Ca-Pb, Ag-Al, Al-Mg, and Fe-Mo all have strong intermetallic compounds in their respective phase systems and when roll bonded provided high initial bond strengths. The post-heat

treatment of these samples, however, resulted in bond strengths all of which approached zero, since the intermetallic compound was formed and observed at the interface. The mechanical strengths of most inter-metallic compounds place them in the brittle class of materials.

In conclusion, we can now expand our list of metallic adhesion variables to include the chemistry of dissimilar contacts and the effects of temperature and diffusion on the interface.

The use of recrystallization as a mode in the mechanism of adhesion has been suggested by several authors (63,64). However, recently Holden et al (65) observed that recrystallization was not involved in the adhesion of Au-Au or Ag-Ag in a series of tests which are quite unique and ought to be expanded upon. Utilizing a very sensitive torsion balance to measure the normal and adhesion forces of electropolished Au and Ag needles on Au and Ag plates, respectively, they showed that the equation:

$$X_o^5 \left[\left(\frac{F}{F_o} \right)^{1/2} - 1 \right]^3 = \left(\frac{81 \sigma \delta a^2}{4k} \right) \left(\frac{Dv}{T} \right) t \quad (15)$$

where:

- X_o = radius of initial contact area
- F_o = breaking force at time zero
- F = breaking force at time (t)
- σ = surface tension
- δ = interatomic jump distance
- a = asperity (needle) radius
- k = Boltzman constant
- Dv = self diffusion coefficient
- T = temperature

was representative of the system by utilizing the data from several adhesion runs to solve Equation (15) for D_v and then comparing these data with those from other self-diffusion experiments. The agreement was quite good. The general observations indicated that recrystallization did not exist but that the interface became a grain boundary which migrated toward its center of curvature, i.e. the needle.

Before opening the discussion of the variables affecting metallic adhesions, there are two more sets of data which ought to be considered since both of these bear directly on the effect of cleanliness of the surfaces in question. A series of adhesion experiments in our laboratory (66,67) were conducted in which two ultra-clean metallic surfaces were brought together under a minimum of normal force and presumably with very low tangential stresses, at room temperature. The observations suggested that miscible metals would adhere and immiscible metals would not as shown in Table III.

TABLE III

Adhesion Results

| <u>Adhesion</u> | <u>No Adhesion</u> |
|-----------------|--------------------|
| Fe-Al | Cu-Mo |
| Cu-Ag | Ag-Mo |
| Ni-Cu | Ag-Fe |
| Ni-Mo | Ag-Ni |

The experiments were conducted under conditions similar to those suggested by Farnsworth (5) in his investigations of ultra-clean surfaces by low energy electron diffraction, that is, the electropolished samples were mounted in a chamber, evacuated to 10^{-11} Torr, argon ion cleaned,

electron beam annealed, re-evaluated to 10^{-11} Torr, and tested. Although adhesion was obscured as a deflection of a Quartz rod and by surface metal transfer as observed under a metallograph, no accurate force measurements were made; thus, the quantitative effects are unknown. Qualitatively, a one to one ratio seemed to fit the observations, e.g. 1 gm. force to make, one gram to break.

Finally, let us look at the recent adhesion data presented by Bryant (68) on mica and graphite. This work examined the forces of cleavage of mica in air and 10^{-13} Torr. The data for mica is shown in Table IV.

TABLE IV

| <u>Mica Cleavage (Bryant)</u> | |
|--|-----------------------------------|
| First Cleavage UHV (10^{-13} Torr) | $\frac{\text{ergs/cm}^2}{10,250}$ |
| Second Cleavage UHV (10^{-13} Torr) | 8,900 |
| Third Cleavage UHV (10^{-13} Torr) | 8,800 |
| Fourth Cleavage UHV (10^{-13} Torr) | 8,620 |
| First Cleavage in air | 300 |
| Second Cleavage in air | 160 |

A careful examination of Table IV provides an excellent guide line in the consideration of the purity problem during adhesion and the extreme effect of adsorbed layers on the reversibility of the system. Firstly, in this experiment, reversibility of atomic coincidence (crystallographic alignment) was in all probability excellent, which meant that a large portion of the surface dipoles were in alignment and adhesion energy did not have to be consumed in interfacial strain of misorientation.

Engineering studies of metal adhesion in vacuum throughout the past few years have been reported in numerous government reports of which those due to the efforts of National Research Corporation (69) and of NASA Ames (70) are of particular interest in that they further demonstrate the necessity of ultra-clean surfaces for exact surface definition, if a correlation of results is expected.

In summarizing the evidence from the various experiments cited above, a degree of caution is suggested in that the force required to fracture an adhesion junction should not be confused with the mechanism of formation of an adhesion junction. This aspect is brought out particularly well in the work of Milner and Rowe in which dissimilar couples, which formed intermetallic compounds, demonstrated strong adhesive bonds until subjected to heat. The heat permitted diffusion and the subsequent formation of an interfacial layer of intermetallic compound which in turn is structurally weak and consequently a general collapse of the bonded system. Although the utilization of such a mechanism might prove valuable in certain friction systems, the force of adhesion (static) is large as opposed to the small force required to cause fracture. An extension of this interpretation is evident in surface contaminants whether present prior to the test or forming after the test due to the migration of impurities to the interfacial area.

Returning again to the ideal system, it is evident from the discussion on physical and chemical adhesion that the fundamental constituents of the bodies in adhesion, i.e. the number of free electrons, ionic size and the nature of the interatomic bonding, determine the nature of

the forces between the respective bodies. Since these same constituents also control the crystal structure, elastic constants, plasticity, surface tension, etc. (18), it should not be surprising that the values of adhesion and adhesion affected parameters (friction, etc.) when plotted against these properties demonstrate a degree of correlation. The correlation between atomic properties of metals and the structure sensitive properties is not usually simple, and, as a consequence, a simple relation involving a non-equilibrium interface between two such materials might be expected to be that much more removed.

Since the results of cold working, radiation bombardment and extreme heating on materials, in general, produces on an atomic level the same effects, i.e. the creation of large numbers of dislocations, vacancies and interstitial atoms which raises the energy level of the system at hand, one might expect that the chemical processes cited in the previous section would proceed with much more rapidity while the physical forces would remain only slightly affected (cf. 11, discussion of temperature effects). With the presence of an increased number of vacancies, diffusion would be permitted to proceed with greater ease provided the activation energy (temperature) were available. If sufficient energy were added to those metallic systems which forms immiscible couples, adhesion would be expected as indicated from their respective phase diagrams.

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EXPERIMENTAL

Throughout the past few years of metallic adhesion research, considerable effort has been expended in the development of a force transfer mechanism that allows accurate, reversible contact force measurements between atomically clean solid surfaces in ultra-high vacuum. As a consequence of these efforts a system has been developed in this laboratory which will provide these requirements at a force level of accuracy (1 part in 500) and a load level (5 gms), which is consistent with the static vacuum techniques in use currently in this laboratory. The system consists of a ten inch torsion balance supported at the center by a 3 mil tungsten wire affixed to two 3/16" stainless steel support arms. One end of the torsion beam contains the sample indenter for adhesion test with a plate specimen fixed to some outside support, i.e. beam support arms. The opposite end of the torsion beam supports a magnet slug affixed to the beam and one end of a 6" straight wire strain gauge (0.95 mil) element. The free end of the strain gauge wire is attached to a second magnetic slug. The glass vacuum cell is constructed such that both magnetic slugs are near the walls and may be interacted upon by magnetic solenoids outside of the system. The field interacting with the slug mounted on the torsion beam is utilized to position the rigid beam such that the indenter sample is almost in contact with the fixed plate sample. Once this is accomplished a force is applied to the second magnetic slug suspended at the end of the strain gauge wire, such that the magnetic lines of force of the positioning magnet are sheared and the rigid torsion beam moves the indenter into contact with the fixed

sample plate. After contact is achieved any additional force applied to the strain gauge magnet is applied directly to the indenter-sample junction with the statics necessary to describe the lever arm action. Contact forces up to 5 gms have been observed with a force resolution of ± 5 mg. In order to measure the force of adhesion for the system the current in the strain gauge solenoid is reduced until the contact breaks. This is possible since the magnetic force of alignment is greater than the strength of the adhesion junction. If the force to make contact is exactly equal to that required to break contact, no adhesion was involved in the system. The system has been shown reproducible in air and in vacuum. (Study of electrical contacts for Sandia Corp. at Syracuse University.) Two such systems are presently in construction for the examination of the effect of composition and temperature on adhesion.

A second system has been designed and is in the early stages of construction, which is expected to shed some light on the nature of the physical adhesion forces between clean metal surfaces. As indicated in the previous section the only conclusive physical adhesion results, which are available, are those for the Quartz-Quartz system in that the chromium, chromium-steel systems, in poor vacuum, yielded very high values at large distances and aluminum yielded repulsion. Since these data do not permit conclusions and an estimate of the magnitude of these forces seems pertinent to a complete adhesion analysis, an experiment was developed. In effect, the forces of attraction between an aluminum plate (containing a freshly condensed aluminum film) and an indenter will be measured on a Cahn electrobalance mounted in the vacuum system. Since

the Cahn balance is always maintained at a balance point due to an electric field on the torsion balance itself and the force, or mass, applied to one arm is proportional to that field, any change in mass in the sample may be recorded on an external electronic recorder without an added change in position of the sample. The second surface (freshly deposited aluminum) will be brought into contact with that mounted on the balance by linearly changing the temperature of a bimetallic strip support. If the approach to contact can be assumed linear and is known, the change in force (balance) vs time recording of the balance can be standardized. The various components of this apparatus are in the last stages of completion. (Note: a General Electric mass analyzer is now available to this project, which will permit a determination of the effect of sorbed gases on physical adhesion).